

A long period grating-based chemical sensor insensitive to the influence of interfering parameters

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Abstract: An optical fibre chemical sensor that is insensitive to interfering parameters including temperature and surrounding refractive index is described. The sensor is based upon a Mach-Zehnder interferometer formed by a pair of identical cascaded long period gratings (LPGs), with the entire device coated with a mesoporous coating of silica nanoparticles. A functional material is infused only into the coating over the section of optical fibre separating the LPGs. The transmission spectrum of the device consists of a channeled spectrum arising from interference of the core and cladding modes within the envelope of the LPG resonance band. Parameters such as temperature, strain and surrounding refractive perturb the entire device, causing the phase of the channeled spectrum and the central wavelength of the envelope shift at the same rate. Exposure of the device to the analyte of interest perturbs only the optical characteristics of the section of fibre into which the functional material was infused, thus influencing only the phase of the channeled spectrum. Measurement of the phase of the channeled spectrum relative to the central wavelength of the envelope allows the monitoring of the concentration of the analyte with no interference from other parameters.

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1. Introduction

Optical fibre long period grating (LPG) based devices offer interesting opportunities for sensing applications due to their inherent sensitivity to a range of environmental perturbations [1]. Typically, the transmission spectrum of an LPG contains a number of resonance bands, each corresponding to coupling of light from the propagating mode of the core of the fibre to a different, co-propagating cladding mode. The wavelengths at which light is coupled from the core to the cladding modes is governed by the phase matching equation [2]

$$\lambda_x = (n_{core} - n_{clad(x)}) \Lambda \quad (1)$$

where, under the assumption of a symmetrical refractive index modulation, λ_x represents the wavelength at which light is coupled to the LP_{0x} cladding mode, n_{core} is the effective refractive index of the mode propagating in the core of the fibre, $n_{clad(x)}$ is the effective index of the LP_{0x} cladding mode and Λ is the period of the LPG. The differential responses of the core and cladding mode effective refractive indices to temperature, strain, bending and surrounding refractive index are manifested as changes in the central wavelengths of the resonance bands. While the simultaneous sensitivity to many parameters presents a challenge when designing sensor systems, each resonance band in the LPG transmission spectrum shows a different sensitivity to each parameter, which has been noted to offer the potential for multi-parameter sensing [1].

There has been considerable interest in the development of chemical sensors based upon long period gratings coated with nanoscale films of chemically sensitive materials. This has been used to sense a range of analytes both in solution and gaseous form, including ammonia [3], ethanol [4] and a range of volatile organic compounds [5]. An issue limiting the practical application of this sensing platform is the sensitivity to temperature, and, when designed for use in solution, to changes in the refractive index of the solution. This issue is exacerbated when the coating thickness and period are chosen such that the LPG is operating near the phase matching turning point (PMT), as the sensitivity to all perturbation is maximised [6,7], and the wavelength separation of adjacent resonance bands is large, requiring a source and spectrometer with large bandwidths to monitor more than one resonance band.

By cascading two identical LPGs it is possible to form an intrinsic fibre optic Mach-Zehnder interferometer (MZI), where the light coupled into the cladding by the first LPG is coupled back into the core by the second LPG to interfere with the light that propagated through the core of the fibre, as illustrated in Fig. 1(a). This produces a sinusoidal channelled spectrum within the resonance bands [8], as illustrated in Fig. 1, for an LPG of period 111 μm fabricated in an optical fibre of cut-off wavelength 670 nm. The phase, ϕ , of the channelled spectrum is dependent on the difference in the optical path lengths of the light propagating in the core and cladding modes, according to [9]:

$$\phi = \frac{2\pi}{\lambda} (n_{core} - n_{clad(x)}) L \quad (2)$$

where λ represents the wavelength, and L is the centre-to-centre distance between two gratings. Perturbation of the section of optical fibre separating the LPGs results in a change in the phase of the channelled spectrum within the resonance band envelope.

As the phase and the resonance wavelength are both dependent upon the difference between the core and cladding mode effective indices, when the entire length of the cascaded LPG is perturbed both the resonance band central wavelength and the phase of the channelled spectrum change at the same rate [10]. This effect can be seen when coating cascaded LPGs with nanoscale films [11]. The authors of [10] used this effect to allow the simultaneous measurement of temperature and strain using cascaded LPGs fabricated in a double clad fibre. The fibre was mounted such that the fibre separating the LPGs could be strained, while the entire length of the device experienced temperature changes. To remove sensitivity to the surrounding refractive index the LPGs were designed such that light was coupled only to the modes of the inner cladding.

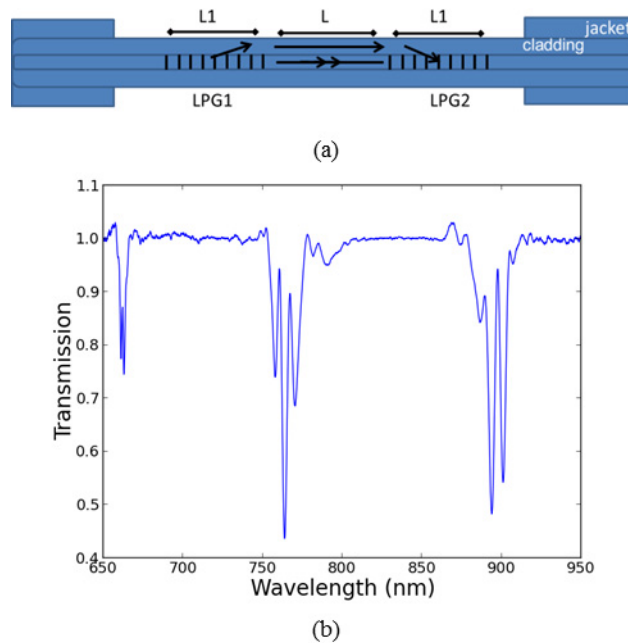


Fig. 1. (a) Schematic diagram of a cascaded LPG Mach-Zehnder interferometer and (b) the transmission spectrum of a pair of near identical cascaded LPGs of length 30 mm and period 110.3 μm , separated by $L = 30$ mm.

Here we describe a chemical sensor based on cascaded LPGs capable of measuring a desired analyte while being immune to the undesired effects of interfering parameters such as temperature and the refractive index (RI) of the fluid surrounding the entire device. The key to this is to coat the entire length of the device with the same base coating but to functionalise only the section of fibre separating the two LPGs. This can be achieved by the use of a porous coating that covers the LPGs and the section of optical fibre separating them, applied for example by the layer-by-layer deposition of a polycation and silica nanospheres [12], as illustrated in Fig. 2. The porous coating over the section of optical fibre separating the LPGs is infused with a functional, chemically sensitive, material [12, 13]. In this way only the section of fibre separating the LPGs will be sensitive to the analyte of interest, with exposure to the analyte causing a change in the phase of the channelled spectrum within the resonance band envelope. Perturbation of the entire length of the device by environmental parameters such as temperature, strain and changes in the refractive index of the fluid containing the analyte causes the central wavelength of the resonance band envelope and the phase of the

channelled spectrum to change at the same rate, assuming that the presence of the functional material does not alter the thermal and refractive index responses of the cladding modes. Thus measurement of the phase of the channelled spectrum with respect to the centre wavelength of the resonance band allows the response to the analyte to be separated from that to interfering parameters.

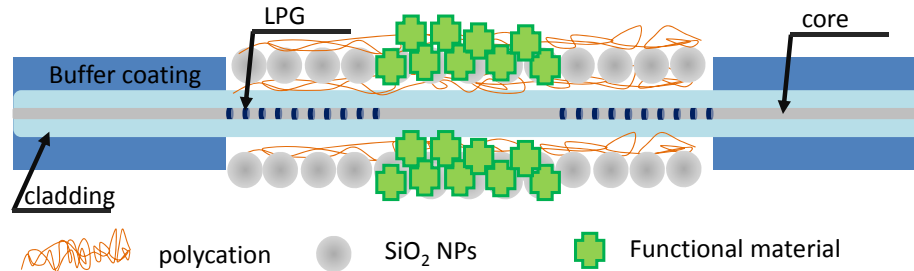


Fig. 2. Schematic of the proposed device. The entire length of the device is coated with a single- or multi- coating of silica nanoparticles, shown here as SiO_2 NPs, to form a porous coating. The functional material is then infused into the length of fibre separating the LPGs.

2. Model

To demonstrate the response of a cascaded LPG pair to perturbation of the LPGs and/or the section of fibre separating the LPGs, the cascaded LPG system was modeled using the approach discussed in [14]. The effective indices of the core and cladding modes were calculated using the technique presented in [15], while the matrix method presented in [9] was used to calculate the transmission spectrum of the cascaded LPG.

The results are illustrated in Fig. 3 for a cascaded LPG pair of period $111\text{ }\mu\text{m}$, separated by 30 mm . The figures in the first column show how the transmission spectrum changes with temperature. In these images, white indicates a transmission of 1, while black represents a transmission of 0. The dark bands allow the movement of the resonance bands across the spectrum to be visualised. The left hand column gives examples of individual spectra to help illustrate the discussion below.

Figure 3(a) shows the response of the resonance band corresponding to coupling to the LP_{017} mode to changes in temperature, from $25\text{ }^\circ\text{C}$ to $125\text{ }^\circ\text{C}$, occurring along the entire length of the device. The thermo-optic coefficients of the core and cladding were assumed differ by 5×10^{-7} [6]. Figure 3(b) shows the response of the device when only the section of fibre separating the LPGs is perturbed. Figure 3(c) illustrates the response of the device where the LPGs experience the same thermal conditions as in Fig. 3(a), but with different perturbation of the temperature of the section of fibre separating the LPGs. In Fig. 3(a) it is clear that both the central wavelength of the resonance band envelope and the phase of the channelled spectrum change at the same rate, while in Fig. 3(b), perturbation of the central section of the LPG induces a change of the phase of the channelled spectrum with no change in the resonance band envelope. In Fig. 3(c), it can be seen that the phase of the channelled spectrum changes at a different rate to that of the envelope. Figures 3(d), 3(e) and 3(f) show individual spectra to clarify the relative movement of the channelled spectra and the resonance band envelope.

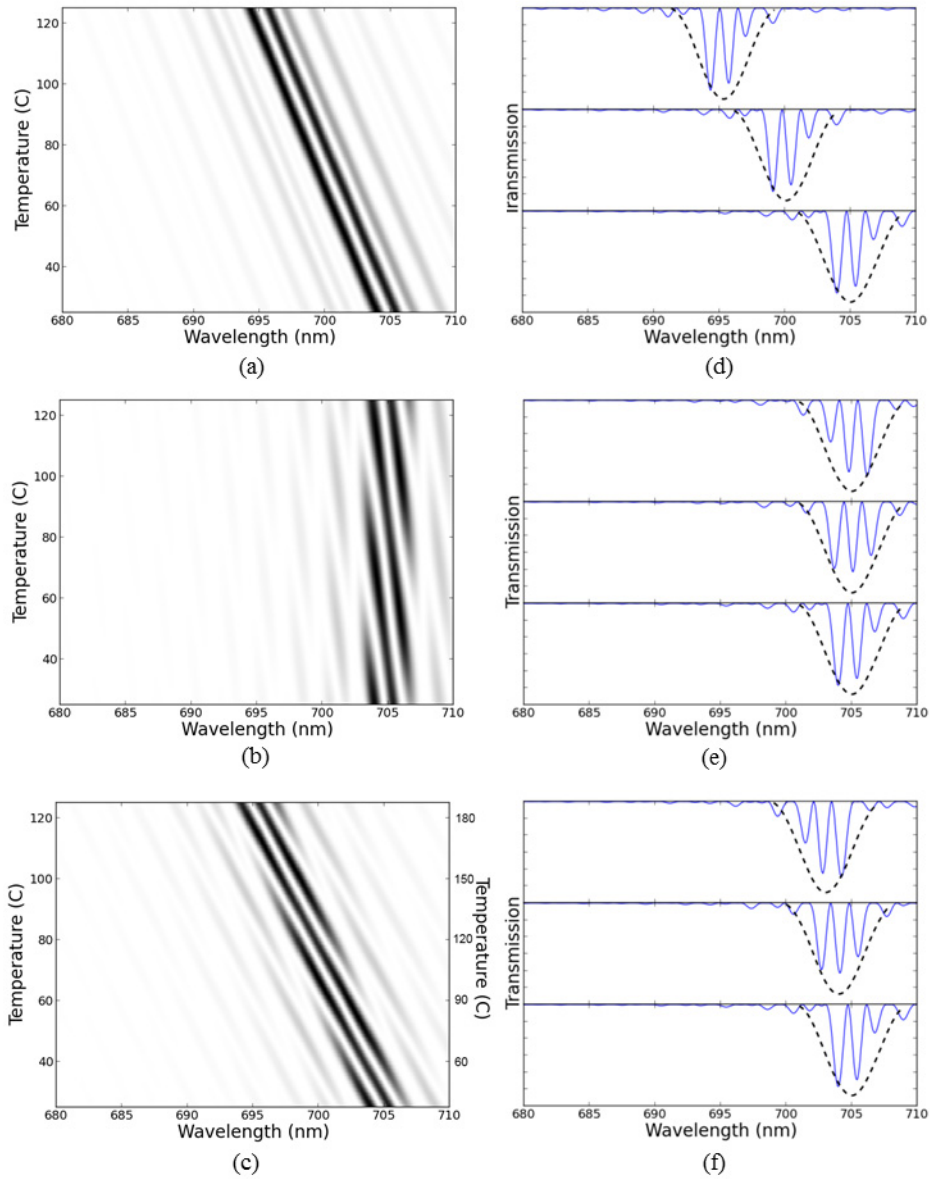


Fig. 3. Plots of the simulated temperature response of the cascaded LPG spectrum of the resonance band corresponding to coupling to LP_{017} , where the LPGs have a period of $111\ \mu\text{m}$. In (a), the temperature changes along the entire device uniformly. In (b) only the length of fibre separating the LPGs is heated while in (c) the temperature over the LPGs is varied differently to that over the section of fibre separating the LPGs. In (c) the left hand Y axis corresponds to the temperature of the LPGs while the right hand Y axis corresponds to the temperature of the fibre separating the LPGs. White represents 100% transmission, and black 0%. Figures 3(d), 3(e) and 3(f) show individual spectra to clarify the relative movement of the channelled spectra and the resonance band envelope. The dotted line represents the envelope of the attenuation bands, determined by modelling a single LPG.

The dispersion of an optical fibre is such that the difference between the core and cladding mode effective indices exhibits a turning point where the value is a maximum. For an LPG fabricated with a period such that Eq. (1) is satisfied at PMTP, it has been shown that

the sensitivity of the transmission spectrum to perturbation is at its maximum, and that for subsequent decreases in $(n_{\text{core}} - n_{\text{clad}(x)})$, the LPG's transmission spectrum is characterised by the formation of a broad resonance band that subsequently splits into two [6]. It has been shown that LPGs operating at this phase matching turning point show their highest sensitivity to changes in the characteristics of nanoscale coatings [7], and also to other parameters [6]. The response of a cascaded LPG pair operating at the phase matching turning point to the conditions described above for Fig. 3 are shown in Fig. 4.

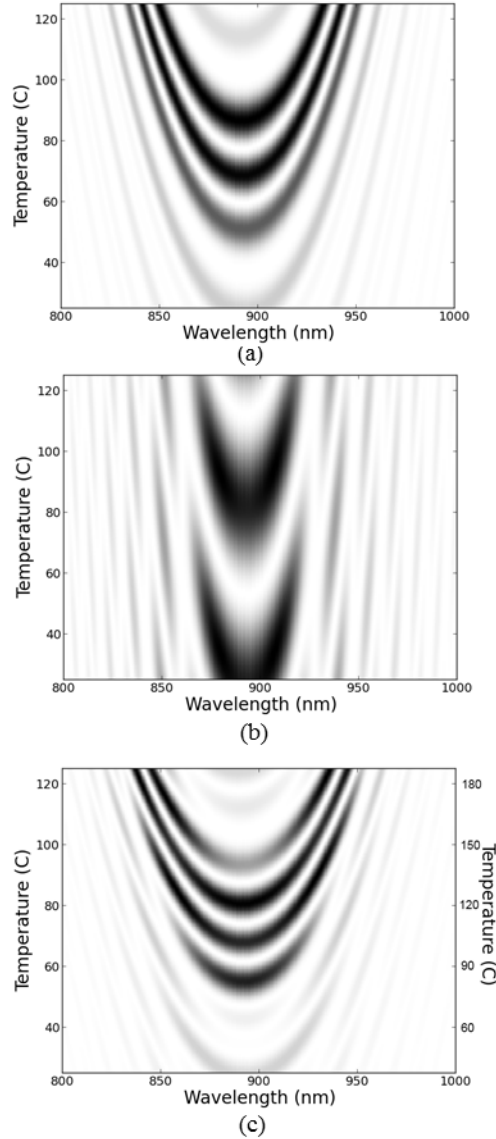


Fig. 4. Plots of the simulated temperature response of the cascaded LPG spectrum of the resonance band corresponding to coupling to LP_{018} , where the LPGs have a period of $111 \mu\text{m}$. In (a) the temperature along the entire device changes uniformly. In 4 (b) only the length of fibre separating the LPGs is heated while in (c) the temperature over the LPGs is varied differently to that over the section of fibre separating the LPGs. In (c) the left hand Y axis corresponds to the temperature of the LPGs while the right hand Y axis corresponds to the temperature of the fibre separating the LPGs. White represents 100% transmission, and black 0%.

Again, both the central wavelength of the resonance band envelope and the phase of the channelled spectrum change at the same rate when the entire device is perturbed, as shown in Fig. 4(a), while the additional perturbation of the central section of the LPG induces a change of the phase of the channelled spectrum with respect to the resonance band envelope, as can be seen in Fig. 4(b).

3. Experiment

3.1 Characterization of the temperature and surrounding refractive index sensitivity of cascaded long period gratings

A pair of identical LPGs, each of period 111 μm and length 30 mm, separated by 30 mm, was fabricated in boron–germanium co-doped optical fibre (Fibercore PS750) with cut-off wavelength 670 nm, in a point-by-point fashion, side-illuminating the optical fibre by the output from a frequency-quadrupled Nd:YAG laser operating at 266 nm. The transmission spectrum of the cascaded LPGs was recorded by coupling the output from a tungsten-halogen lamp (Ocean Optics HL-2000) into the optical fibre and by analysing the transmitted light using a fibre coupled CCD spectrometer (Ocean Optics HR4000). The grating periods were selected such that the LPGs operated near the phase matching turning point, which, for coupling to a particular cladding mode (in this case LP_{018}), ensures optimised sensitivity to changes in the properties of a coating deposited onto the LPG [7]. The response of the device to perturbation of different sections of the cascaded device was investigated. This involved exposing, in turn, the section separating the LPGs and the whole structure (both LPGs and the section of optical fibre separating them) to temperature and RI changes. When investigating the response of the device to temperature, two configurations were used. When considering changes over the section of optical fibre separating the LPGs, this section of fibre was placed into a calibrated tube furnace of length 25 mm. To characterise the thermal response of the entire length of the cascaded LPG device, the cascaded LPGs were placed in an oven, along with a temperature data logger (DS1923 temperature/humidity logger iButton®, range -20 to $+85^\circ\text{C}$, resolution 0.5°C). To investigate the response of the device to changes in the surrounding RI, the appropriate sections of the LPG pair was immersed into water and ethanol solution with different concentrations with corresponding RI values ranging from 1.33 to 1.36. This was achieved using a PTFE holder which contained three wells of appropriate length, into which the ethanol solution could be introduced, as required.

Figures 5(a) and 5(b) show the response of the resonance bands of the cascaded long period grating pair when the central section of the device experienced changes in temperature. The phase of the channelled spectrum changed, while the resonance band envelope remained fixed. This can be seen for the resonance bands corresponding to coupling to the LP_{018} cladding mode (at the PMTP) and LP_{017} mode resonances. When both the LPGs and the section of fibre separating them experienced the same temperature change, the LP_{018} resonance band operating at the PMPT is observed to form and split into two, as shown in Fig. 5(c). The phase of the channelled spectrum can be seen to change at the same rate, remaining constant relative to the central wavelength of the resonance band envelope. The LP_{017} resonance band suffers a blue shift with increasing temperature, and again the channelled spectrum phase changes at the same rate as the envelope, as can be seen in Fig. 5(d).

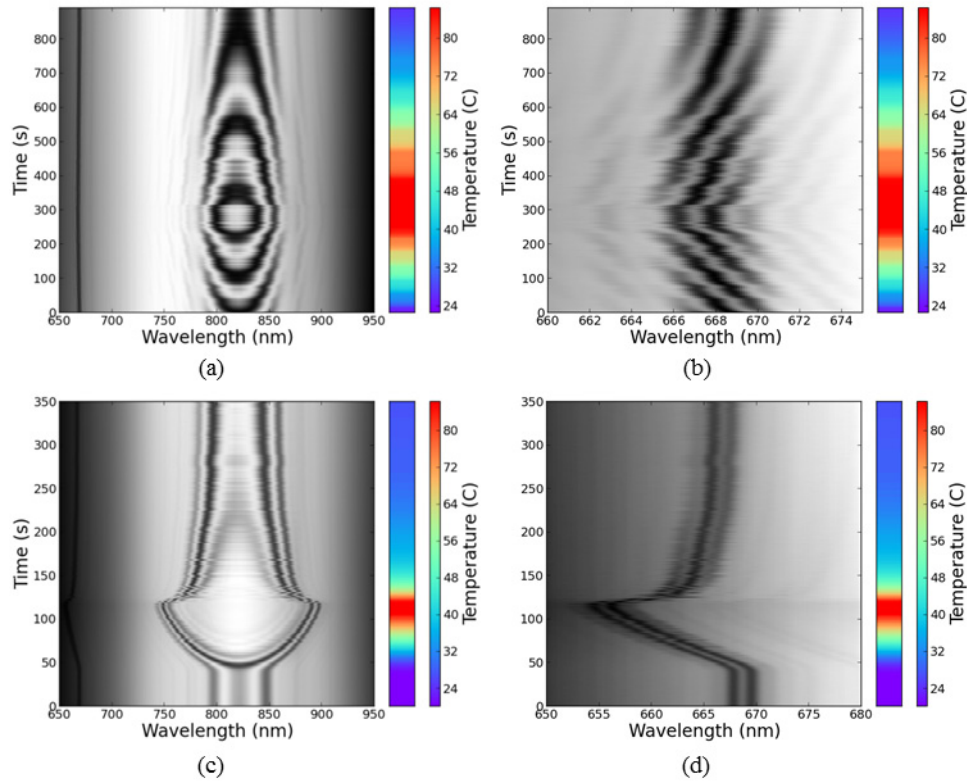


Fig. 5. The temperature response of the transmission spectrum of the cascaded LPG pair. (a) shows the resonance bands corresponding to coupling to both the LP_{017} (shorter wavelength band) and LP_{018} (longer wavelength band) modes when the section of fibre separating the LPGs was heated/cooled, with (b) focusing on the response of band corresponding to coupling to LP_{017} . (c) and (d) show the responses of these bands when the length of the entire device was heated/cooled. The white and black correspond to transmission values of 100% and 0%, respectively. The colour bar immediately to the right of the grey-scale plot shows the temperature.

Similar effects were observed when the cascaded LPG was exposed to changes in the surrounding refractive index, as shown in Fig. 6(a) where, on changing the surrounding refractive index by varying the concentration of a solution of ethanol around the entire device, the resonance band wavelength and the channelled spectrum phase were observed to shift at the same rate. When only the section of optical fibre separating the LPGs was immersed into an ethanol solution, the envelope did not shift but changes of the phase of the channelled spectrum were observed, as can be seen in Fig. 6(b).

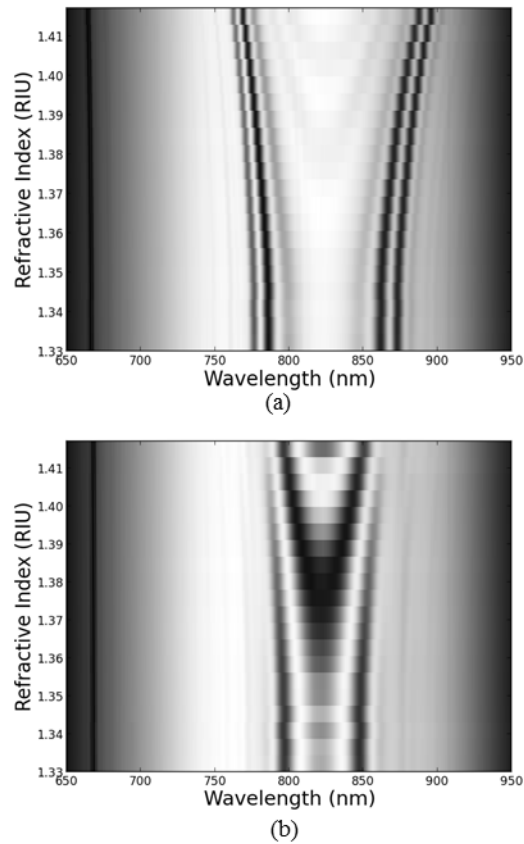


Fig. 6. (a) Transmission spectra of a cascaded LPG pair with grating period $111\ \mu\text{m}$, measured when (a) the RI of the material surrounding the entire device was changed and (b) when only the section of optical fibre separating the LPGs was exposed to different RI values.

3.2 Chemical sensor characterisation

In [11] we presented a two-stage technique for the fabrication of LPG-based chemical sensors. The 1st stage involves the deposition of a mesoporous coating of silica nanospheres onto the cladding of the optical fibre using the layer-by-layer electrostatic self-assembly technique. In the 2nd stage the functional material is infused into the mesoporous coating. Here, the optical fibre containing the cascaded LPG pair described in section 3.1 was rinsed with deionized water and immersed into a 1 wt% ethanolic KOH (ethanol/water = 3:2, v/v) for 20 min, producing a negatively charged surface. The optical fiber was then immersed sequentially into an aqueous solution of a positively charged polymer, poly(diallyldimethylammonium chloride) (PDMA, Mw: 200000–350000, 20% w/w in H_2O) and into an aqueous solution containing negatively charged SiO_2 NPs (SNOWTEX 20L, Nissan chemical industries), each for 20 min, so that alternate layers of PDMA and SiO_2 were deposited onto the optical fiber's surface. The optical fiber was rinsed with distilled water, and dried by flushing with nitrogen gas after each deposition step. This was repeated 10 times to produce a film of thickness of order 400 nm. The section of the coated optical fibre separating the LPGs was then immersed into a solution of tetrakis-(4-sulfophenyl)porphine (TSPP), a functional material that we have shown previously to be suitable for use on the LPG sensing platform to develop ammonia sensors [3]. Figure 7 shows the evolution of the transmission spectrum of the cascaded LPG pair as the TSPP infused into the section of

mesoporous coating covering the length of fibre separating the LPGs. This was achieved using the PTFE holder described above and adding the TSPP solution to only the central well.

The change in phase of the channeled spectrum is a result of the increase in the refractive index of the mesoporous coating as the TSPP binds to the silica nanospheres. The central wavelength of the resonance band envelope is unchanged. After 460 s, the channeled spectrum disappears and only the resonance band envelope remains. When out of the solution and dried, the visibility of the channeled spectrum returned to that observed prior to infusion, but with a phase shift indicative of the refractive index change of the TSPP infused section of the mesoporous coating, as shown in Fig. 7(b). This behaviour is attributed to a combination of the high refractive index of the TSPP infused mesoporous coating and to the refractive index of the surrounding solution. This has been observed previously for the infusion of TSPP into mesoporous coated LPGs, where the resonance bands' extinction ratios reduced during the infusion of the TSPP, but the bands reappeared when out of the solution and after drying, with a wavelength shift compared that measured prior to TSPP infusion [3].

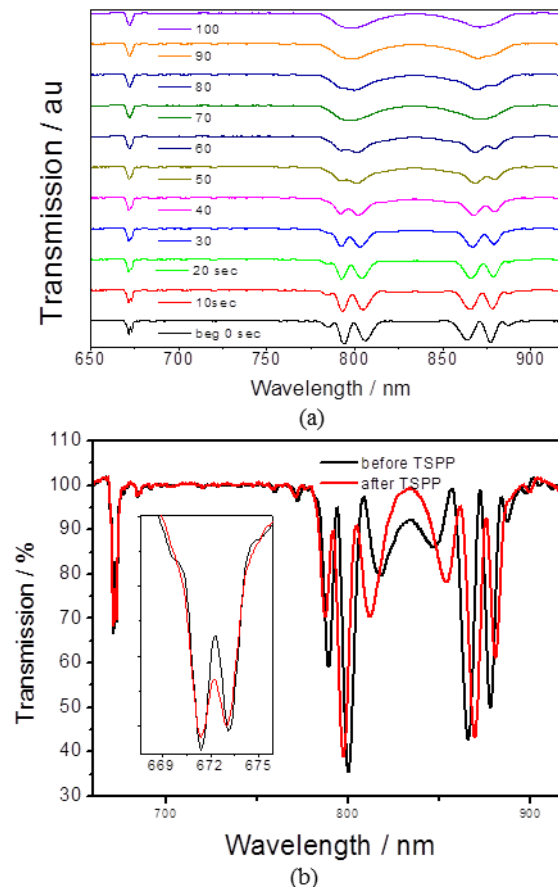


Fig. 7. (a) Evolution of the transmission spectra of the cascaded LPG pair as the TSPP infused into the mesoporous coating over the section of optical fibre separating the LPGs, recorded in solution. (b) Transmission spectra recorded before and after infusion of TSPP, recorded in air.

Figure 8 shows the temperature response of the entire length of the mesoporous coated cascaded LPG-pair, with the section of fibre separating the LPGs infused with TSPP. As can be seen, the phase of the channeled spectrum and the central wavelength of the resonance band envelope change at the same rate, suggesting that any possible thermo-optic response of the TSPP did not influence the phase of the channeled spectrum. The discontinuities at

approximately 600 s and 2250 s are a result of sudden changes in the temperature caused by opening the door of the oven. When the entire length of the device was immersed in sucrose solutions of different concentrations (and thus refractive indices) the spectra shown in Fig. 9 were recorded.

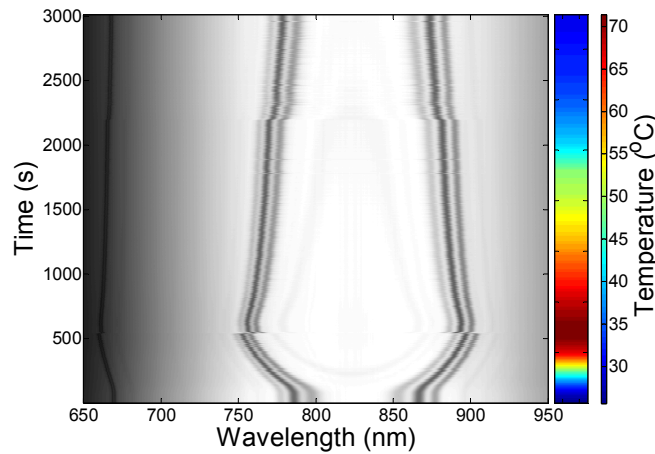


Fig. 8. Evolution of the transmission spectrum of the cascaded LPG with mesoporous coating (with the coating over the length of fibre separating the LPGs) in response to changing the temperature along the length of the entire device.

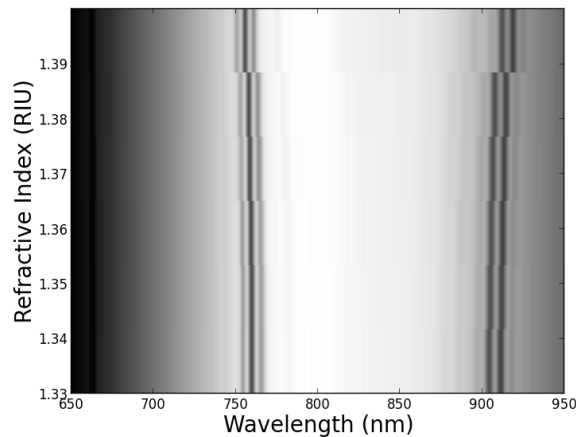


Fig. 9. Evolution of the transmission spectrum of the device in response to a change in the surrounding RI.

Again, the phase of the channelled spectrum and the central wavelength of the resonance band envelope change at the same rate, and the increase refractive index of the TSPP-infused section of coating does not influence the response of the cladding modes to changes in surrounding refractive index.

To demonstrate the use of this device as a sensor, it was exposed to NH_3 vapour. Figure 10(a) shows a change of phase of the channelled spectrum with respect to the envelope, indicating that the TSPP infused central section of the device is changing its refractive index in response to the NH_3 vapor, consistent with our previous observations [3]. We have previously demonstrated that TSPP forms *J*-aggregates in the mesoporous thin film and exposure to ammonia deprotonates the pyrrole ring of the porphyrin leading to the distortion of the *J*-aggregation accompanied by the changes in the absorption spectra and RI [3]. Exposure of the TSPP compound to HCl produces the opposite effect: the protonation of the TSPP and formation of *J*-aggregates with concomitant increase of the RI. Figure 10b shows the changes in the form of the transmission spectrum when the device was exposed of the

device to the HCl vapour. The change of phase of the channeled spectrum with respect to the envelope suggests an increase of the RI of the central section modified with TSPP.

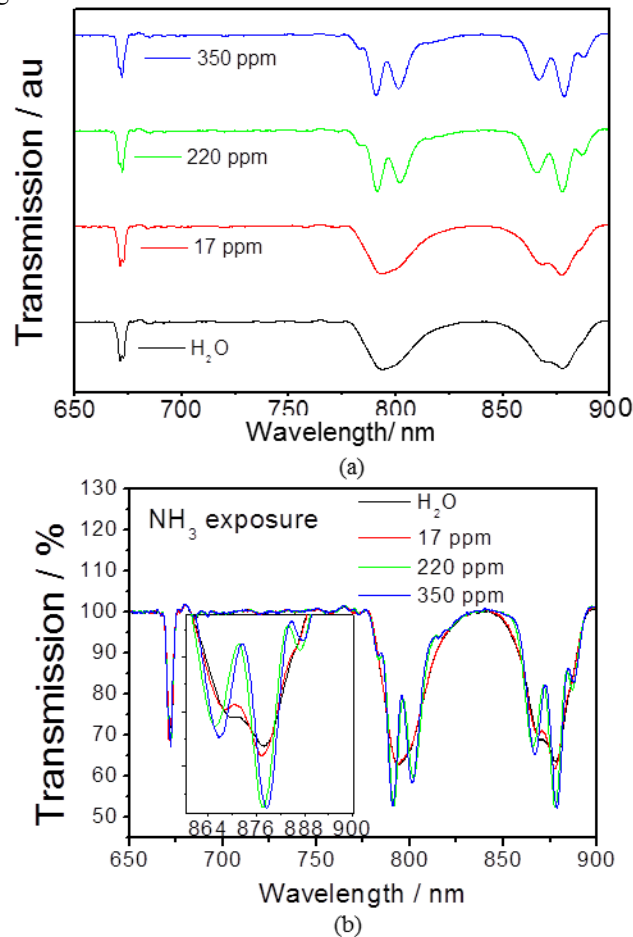


Fig. 10. Evolution of the transmission spectrum of the device on the exposure to (a), water and ammonia of different concentrations and (b), HCl vapour, for different time intervals.

4. Conclusions

The response of the transmission spectrum of a cascaded LPG pair to environmental perturbations has been investigated theoretically and experimentally. It has been shown that, when the perturbation is applied along the entire length of the device, the channeled spectrum and the resonance band envelope shift in wavelength at the same rate. When the section of fibre separating the LPGs is perturbed, only the channeled spectrum is affected. This effect has been used to demonstrate a chemical sensor that is insensitive to the interfering effects of temperature and surrounding refractive index. The cascaded LPG device is coated with a mesoporous coating of silica nanospheres. The coating over the section of fibre separating the LPGs is infused with a functional material, in this case TSPP, a material whose refractive index is sensitive to exposure to ammonia. Temperature and surrounding refractive index changes perturbed both the envelope and the channeled spectrum equally, while exposure to ammonia influenced only the channeled spectrum.

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